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(54) Title: ISOCYANATE MODIFIED CELLULOSE PRODUCTS AND METHOD FOR THEIR MANUFACTURE

(57) Abstract

A method is disclosed for producing a polyurea-cellulose composite material from substantially delignified cellulosic material and an isocyanate resin. The isocyanate resin comprises a polyisocyanate, preferably PMDI, and a miscible organic solvent, preferably one such as propylene carbonate having a high boiling point and low flammability and toxicity. The composite surprisingly exhibits values of physical parameters that are at least as good as, and sometimes far superior to, corresponding parameters of similar composites made using neat (undiluted) polyisocyanate. Single- and multiple-ply composites can be made, employing only a single curing step.

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ISOCYANATE MODIFIED CELLULOSE PRODUCTS AND METHOD FOR THEIR MANUFACTURE

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CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of co-pending U.S. application Serial No. 07/275,824, filed November 25, 1988.

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FIELD OF THE INVENTION

This invention relates generally to a composite material comprising a matrix of cellulose fibers impregnated with a synthetic polymer. More particularly, it relates to a composite material comprising one or more plies of pulped or delignified cellulose fibers with a binder comprised largely of polyurea.

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BACKGROUND OF THE INVENTION

Polyisocyanates have had wide study as adhesives and binders in forming composite materials. For example, polyisocyanates have been used to manufacture composite wood products such as a hardboard and particleboard. Each such product has a defined scope of industrial utility, rendering it useful for 20 certain applications but not others.

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U.S. Patent No. 3,666,593 to Lee discloses a method for making rigid panels comprising a rigid substrate overlaid with one or more layers of polyisocyanate-impregnated paper. Candidate substrates are wood, metal, plastic, or asbestos board. Lee teaches that at least 30% (up to about 150%) w/w polyisocyanate resin, relative to the mass of the paper, is required to yield a satisfactory paper-overlay panel. Lee also teaches that the polyisocyanate-impregnated paper should be cured at a pressure ranging from 100 to 35 psi and at a temperature within the range 280 to 340°F.

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U.S. Patent No. 4,359,507 to Gaul et al. discloses an adhesive binder composition suitable for lignified cellulose for manufacturing composite materials such as flakeboard or particleboard. The binder comprises a polyisocyanate and

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an amount of a mixture of ethylene carbonate, propylene carbonate, and optionally extraneous lignin sufficient to lower the viscosity of the binder. The amount of polyisocyanate is within the range of 20 to 95% w/w, preferable 50 to 75% w/w, relative to the mass of the mixture of polyisocyanate and carbonate.

5 The purpose of the carbonates and optional lignin is to reduce the viscosity of the binder. A less viscous binder is apparently easier to apply to lignified cellulose particles such as wood chips and the like during a milling, mixing, or tumbling operation. The carbonates and lignin also serve as extenders to reduce the requisite amount of relatively expensive polyisocyanate needed for satisfactory 10 binding together of the lignocellulose particles.

U.S. Patent No. 4,486,557 to Gaul et al. discloses an adhesive binder composition for lignified cellulose comprising a mixture of a polyisocyanate, an epoxide, and lignin. Suitable lignified celluloses include wood chips and the like as in the U.S. '507 patent. The lignin and epoxide serve as diluents and 15 extenders for the polyisocyanate.

U.S. Patent No. 4,344,798 to Gaul et al. is similar to the U.S. '557 patent except that the binder comprises a polyisocyanate and a dialkyl ester of carbonic acid and optionally lignin. The latter two ingredients serve as extenders for the polyisocyanate.

20 U.S. Patent No. 4,361,622 to Gaul et al. is similar to the U.S. '557 patent except that the binder comprises a polyisocyanate-alkylene oxide or halogenated alkylene oxide. Again, the additional ingredients serve as polyisocyanate extenders to reduce cost.

25 U.S. Patent No. 4,414,361 to Gaul et al. is similar to the U.S. '507 patent except that the binder includes, along with a polyisocyanate, a cyclic alkylene carbonate and optionally lignin as extenders to reduce the requisite amount of costly polyisocyanate.

30 A portion of the teachings of Gaul et al. as disclosed in the U.S. '662 and '361 patents is summarized in Gaul et al., "Novel Isocyanate Binder Systems for Composite Wood Panels," Proceedings of the S.P.I. International Technical/Marketing Conference, San Diego, California, Nov. 2-4, 1983,

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pp. 389-407. In that report, propylene carbonate is described as an "effective diluent" for isocyanates, offering distinct "cost advantages" when used with a polyisocyanate such as poly(diphenylmethane diisocyanate) ("PMDI") in, for example, a 70% PMDI/30% propylene carbonate binder system. That report also 5 summarized certain physical properties of propylene carbonate, such as a high boiling point of 242°C (at 760 mmHg) and a high flash point of 132°C. Further, that report teaches that dilution of PMDI with organic liquids miscible in the polyisocyanate, such as propylene carbonate, yields particleboards exhibiting 10 decreased internal bonding strength, where the greater the percent of propylene carbonate relative to the PMDI, the lower the internal bonding strength. PMDI dilution also results in decreased modulus of rupture and modulus of elasticity.

Finally, European patent application No. 0,304,273 to Younes discloses laminate composite materials in which at least one substance such as metal, cellulose, plastic, glass, or ceramic is compression-molded with a "reaction 15 mixture" of a polyisocyanate and a cyclic alkylene carbonate. The amount of cyclic alkylene carbonate is within the range of 2 to 50% w/w, preferably 20 to 35% w/w, relative to the mass of the isocyanate-carbonate mixture. The "reaction mixture" also includes a special catalyst comprising a soluble adduct of a tertiary amine and a cyclic alkylene carbonate. Cellulosic composites producible 20 according to this publication include woodlike materials and particleboards. The polyisocyanate component of the "reaction mixture" apparently forms a rigid polyisocyanurate thermoset rather than a polyurea.

Hence, the prior art teaches various schemes for producing 25 composites from cellulosic materials and polyisocyanate, where a miscible compound in the reaction mixture such as propylene carbonate or other organic liquid serves as an extender or diluent, allowing the use of lesser amounts of costly polyisocyanate. While the prior art suggests that it is desirable to add as much extender as possible from the standpoint of cost, the maximal amount of extender relative to the amount of polyisocyanate is limited, according to the 30 prior art, by the maximum allowable compromise in physical properties of the composite resulting from diluting the polyisocyanate. In other words, the prior

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art teaches that diluting the polyisocyanate, while lowering manufacturing costs of particleboards and the like, also yields decreased values of important physical parameters such as internal bonding strength, modulus of rupture, and modulus of elasticity. As a result, composites made according to the teachings of the prior art, while having a certain range of useful properties, lack utility for other important industrial uses.

Accordingly, there is a need for industrially useful composites of polyurea and cellulosics other than wood chips and the like, particularly composites comprising substantially delignified fibrous cellulose fillers such as paper-like materials.

There is also a need for such composites wherein the mass percentage of the polyurea is small relative to the mass of the cellulosic material, such as 20% w/w or less.

There is also a need for a process for making such composites wherein the polyisocyanate can be diluted with a miscible organic solvent to reduce manufacturing costs, while still forming a composite having physical properties that are equal to or exceed the corresponding physical properties of similar composites made using more costly undiluted polyisocyanate.

There is also a need for such composites having a substantially uniform distribution of polyurea throughout, even when the polyisocyanate is applied as a liquid resin to the outside surfaces of the substantially delignified cellulose and must subsequently penetrate into the interior matrices of the cellulose material before the polyisocyanate is cured to form the composite.

There is also a need for such composites that can be made having multiple plies each comprised of substantially delignified cellulose and polyurea, where the distribution of polyurea is substantially uniform throughout the composite.

SUMMARY OF THE INVENTION

In accordance with the present invention, a polyurea-cellulose composite material is produced from a substantially delignified cellulosic material

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and an isocyanate resin comprising at least one polyisocyanate compound diluted with an organic solvent miscible with the polyisocyanate. The solvent constitutes a maximum of about 20% w/w of the polyisocyanate and the isocyanate resin constitutes about 8-20% w/w of the cellulosic material. The cellulosic material, 5 which preferably has a maximum moisture content of 7% w/w, is uniformly impregnated with the resin, then cured at a temperature within a range of about 105°-245°C for five minutes or less at a pressure of about 130-1200 psig.

The polyurea-cellulose composite can comprise single or multiple plies or laminae of polyisocyanate-impregnated cellulosic material. To produce 10 a plied composite, the impregnated laminae, before curing, are arranged into a laminarily stacked configuration before application of heat and pressure.

The polyisocyanate is preferably poly(diphenylmethane diisocyanate) but can be selected from the group consisting of lower aliphatic, alicyclic, and aromatic polyisocyanates, and mixtures thereof. The solvent is preferably 15 propylene carbonate but can be selected from the group consisting of alkylene carbonates, aromatics, halogenated aromatics, ethers, ketones, and alkyl acetates. If desired, a catalyst can be used, selected from the group consisting of aliphatic tertiary amines, aliphatic metal complexes, and acetyl acetonates, at a concentration in the isocyanate resin of about 0.1 to about 0.5% w/w. The 20 cellulosic material is selected from the group consisting of pulped cellulose fibers, chemical pulps, thermomechanical pulps, bleached and unbleached paper and paper-like materials, non-woven mats, sheets and felts.

With a view to departing from the above-disclosed disadvantages of the prior art, a key object of the present invention is to provide a method for 25 making a composite of substantially delignified cellulose and polyurea requiring lesser amounts of polyisocyanate than prior-art methods, relative to the cellulosic material, while having important physical parameters at least as good as, if not superior to, composites made using prior-art methods.

Another object is to provide such a method wherein the distribution 30 of polyurea throughout the composite is substantially uniform to ensure high values of such parameters as internal bond strength.

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Another object is to provide such a method wherein the isocyanate resin becomes uniformly distributed through the thickness dimension of the impregnated cellulosic material, even when the resin is applied to the surfaces of the cellulosic material.

5 Another object is to provide such a method wherein the polyisocyanate is diluted using a solvent having low flammability and toxicity, and high boiling point.

10 Another object is to provide such a method wherein a multiple-ply polyurea-cellulose composite can be manufactured by impregnating multiple laminae of cellulosic material and curing the plied laminae in a single curing step.

Another object is to provide panels and other shapes comprising a polyurea-cellulose composite made according to the present invention and usable for a large variety of industrial applications.

15 The foregoing objects and other features and advantages of the present invention will be more fully understood as the detailed description thereof proceeds, particularly when considered together with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWINGS

20 Figure 1 is a histogram showing the effects of various amounts of propylene carbonate on the viscosity of PMDI polyisocyanate.

Figure 2A is a sectional view of a polyurea-cellulose composite made by impregnating a kraft linerboard with neat PMDI; felt side is on top, wire side on bottom; 60X magnification.

25 Figure 2B is a sectional view as in Figure 2A, but where the PMDI was diluted by adding 5% w/w propylene carbonate, relative to the PMDI.

Figure 2C is a sectional view as in Figure 2A, but where the PMDI was diluted by adding 10% w/w propylene carbonate, relative to the PMDI.

30 Figure 2D is a sectional view as if Figure 2A, but where the PMDI was diluted by adding 15% w/w propylene carbonate, relative to the PMDI.

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Figure 3 is a histogram showing the distribution of polyurea (as % nitrogen) through the "Z" or thickness dimension of a polyurea-cellulose composite when PMDI, in either neat form or dissolved in acetone (13% w/w), was applied on one or both sides of a kraft linerboard.

5 Figure 4A is a plot of internal bond strength of a 3-ply polyurea-cellulose composite made with 58-lb basis-weight kraft linerboard impregnated with neat or propylene carbonate-diluted PMDI in the presence or absence of a catalyst.

10 Figure 4B is a plot similar to Figure 4A except that the kraft linerboard was 69-lb basis weight.

Figure 5A is a plot of tensile strength, in the machine direction, of a 3-ply polyurea-cellulose composite made with 58-lb basis-weight kraft linerboard impregnated with neat or propylene carbonate-diluted PMDI in the presence or absence of a catalyst.

15 Figure 5B is a plot similar to Figure 5A but showing percent elongation of the composite at time of fracture during the tensile testing shown in Figure 5A.

Figure 5C is a plot similar to Figure 5A except that the kraft linerboard was 69-lb basis weight and no catalyst was used.

20 Figure 5D is a plot similar to Figure 5B except that the kraft linerboard was 69-lb basis weight and no catalyst was used.

25 Figure 6A is a plot of modulus of rupture, in the machine direction, of a 3-ply polyurea-cellulose composite made with 58-lb basis-weight kraft linerboard impregnated with neat or propylene carbonate-diluted PMDI in the presence or absence of a catalyst.

Figure 6B is a plot similar to Figure 6A except that the kraft linerboard is 69-lb basis weight and no catalyst was used.

30 Figure 6C is a plot of modulus of elasticity, in the machine direction, of a 3-ply polyurea-cellulose composite made with 58-lb basis-weight kraft linerboard impregnated with neat or propylene carbonate-diluted PMDI in the presence or absence of a catalyst.

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Figure 6D is a plot similar to Figure 6A except that the kraft linerboard is 69-lb basis weight and no catalyst was used.

DETAILED DESCRIPTION

5 The cellulosic material comprises cellulose fibers from the group consisting of substantially delignified cellulose fibers, including pulped fibers, "chemical pulps," "thermomechanical pulps," recycled pulp fiber, bleached and unbleached paper and paper-like materials, non-woven mats, sheets or felts, and the like. The origin of the delignified cellulose can be any of a large variety of
10 sources, including wood and various other plant fibers, such as from agricultural by-products, and also including recycled cellulose. Delignified celluloses are characterized as having had most to substantially all the indigenous lignin and analogous naturally-occurring binders removed. Delignification increases the opportunity for reaction between isocyanate groups on molecules comprising the
15 resin and the hydroxyl groups present on cellulose molecules.

For convenience, the cellulosic material is preferably in a substantially two-dimensional or sheet form having sufficient porosity to absorb liquids. Sheets, compared to other shapes, are generally easier to impregnate with a liquid using conventional machinery. However, three-dimensional forms
20 of cellulosic material may also be impregnated, including complex shapes. The principal limitation on shape is dictated by available machinery for controllably impregnating the cellulosic material and for subsequently curing the impregnated material in a uniform manner using heat and pressure.

25 A preferred cellulosic material is "kraft linerboard," which is a paper-like board made according to the kraft (sodium sulfate) method of papermaking. Linerboards are commonly used for the outer layers of a corrugated board used, for example, in the construction of shipping cartons. Such sheets are manufactured in a number of basis-weight grades, ranging from about 30 lb basis weight (30 lb/1000 ft²) to about 90 lb basis weight (90 lb/1000 ft²).

30 The cellulosic material preferably includes a small amount of moisture, up to about ten percent w/w relative to the mass of cellulose. Such a

level of moisture is not generally detectable in a tactile sense as "wetness." Rather, water molecules comprising such moisture are tightly associated with the cellulose molecules as one or more molecular layers of water present on the cellulose fibers. Such moisture is normal with cellulosics because of the hydrophilic nature of cellulose. Hence, it is usually not necessary to add extraneous moisture. However, under extremely arid conditions, adding moisture to the cellulose fibers by, for example, application of steam, may result in improved impregnation of the resin.

The moisture will serve as a reactant, since water is known to react with isocyanates. This is supported by the fact that some residual moisture in the cellulosic material seems to improve the qualities of the composite. Also, infrared spectral analyses of various composites made according to the present invention indicate that urethanes are formed when the resin and the cellulosic material are anhydrous at the time of curing. No urethane peaks are observed when moisture is present. The presence of moisture has also been found to yield faster curing than no moisture at all (anhydrous).

The preferred polyisocyanate compound is poly(diphenylmethane diisocyanate) (referred to herein as "PMDI"), such as PAPI-2027 available from Dow Chemical Corporation, Midland, Michigan. PMDI is a partially polymerized, or "oligomerized," material. Other organic polyisocyanates are also usable, simply by virtue of such compounds possessing at least two isocyanate (-NCO) groups per molecule, which renders the molecules polyfunctional and capable of reacting to form crosslinked polymeric materials. Hence, candidate polyisocyanates include lower (C_1 - C_{12}) aliphatic, alicyclic, and aromatic polyisocyanates. Polyisocyanates may be used as single compounds or mixtures or two or more different polyisocyanate compounds.

The organic solvent used as a diluent for the polyisocyanate must be miscible with the polyisocyanate. The resulting liquid mixture is termed herein a "resin." The preferred solvent is propylene carbonate, principally because it is substantially odorless and colorless, has low viscosity, low toxicity, low vapor pressure at room temperature, and low flammability (boiling point: 242°C;

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flashpoint: 132°C). The high boiling point of propylene carbonate is particularly advantageous because this solvent is thereby prevented from vaporizing under curing conditions of elevated temperature and pressure. Boiling during curing can cause undesirable formation of bubbles in the polyurea, resulting in a 5 composite having unacceptable appearance and physical properties. The high flash point of propylene carbonate is an important indicator of its low flammability. Other organic solvents can also be used, so long as drawbacks of those other organic solvents, such as toxicity, low boiling point, or flammability, can be accommodated. Candidate alternative solvents include, but are not 10 limited to, aromatics such as benzene, halogenated benzenes, nitrobenzenes, alkylbenzenes such as toluene and xylenes, halogenated lower aliphatics, ethers, ketones, alkyl acetates, and other alkylene carbonates.

One benefit of diluting the polyisocyanate with an organic solvent is reduced cost, since polyisocyanates such as PMDI are relatively expensive 15 compared to the cost of the solvent. Also, and very importantly, up to about 20% w/w solvent in the resin, relative to the polyisocyanate, confers surprisingly improved mechanical properties to the polyurea-cellulose composite of the present invention, compared to similar composites made using "neat" (undiluted) polyisocyanate (see Examples). These improved properties become apparent 20 when the amount of solvent is at least about 5%. An amount of solvent greater than about 20% w/w, while sometimes also yielding improved mechanical properties over neat polyisocyanate, can yield a composite exhibiting an unacceptably high degree of water-absorption. Hence, about 20% w/w solvent is regarded herein as a practical upper limit and about 5% w/w is regarded as a 25 practical lower limit. A greater relative percentage of solvent (20 to 50% w/w) may be required, however, to achieve satisfactory impregnation of such cellulosics as bleached fluff pulp fiber sheets that are difficult to impregnate with a more viscous polyisocyanate resin having less solvent.

It is not entirely clear what role the organic solvent plays in 30 conferring improved mechanical properties to the composite. One possible mechanism is that addition of a low-viscosity solvent tends to reduce the viscosity

of the relatively viscous polyisocyanate. Reduced viscosity appears to yield improved penetration of the resin into the physical matrix presented by the cellulosic material (see Example 2). The solvent may also confer benefits due to solvation effects which, in turn, enhance the reactivity of the polyisocyanate with 5 cellulose molecules. For example, solvation may result in improved "wetting" of cellulose fibers by the polyisocyanate, or may lower the energy of reaction between polyisocyanate and cellulose molecules, thereby allowing more bonding reactions per unit volume to occur between polyisocyanate and cellulose at a given temperature and pressure. Solvation may also facilitate reaction of the 10 polyisocyanate with residual water molecules. It is likely that more than one of these effects of adding solvent are responsible for the improved mechanical properties of the composite.

Propylene carbonate may serve as a copolymerizable reactant with the polyisocyanate to some limited extent. This solvent has been reported to 15 react in the presence of a catalyst with organic polyisocyanates to form isocyanurates under certain conditions. See Tzuzuki et al., "New Reactions of Organic Isocyanates. I. Reaction with Alkylene Carbonates," J. Org. Chem. 25:1009 (1960). Absence of such copolymerization reactions with PMDI in the present instance is indicated by the absence in the composite of an isocyanurate 20 IR absorption spectral pattern. Other solvents, however, may react with polyisocyanate.

To prepare the resin, it is merely necessary to add the requisite amount of organic solvent to the corresponding amount of polyisocyanate, within the range of about 5% to about 20% w/w solvent relative to the mass of the 25 polyisocyanate. Combining the polyisocyanate and the solvent can be performed by a batch or continuous process using equipment generally known in the art.

The resin is preferably prepared and cured without an added catalyst, although a catalyst can be added without departing from the principles of the present invention. As is known in the art, a catalyst enhances a chemical 30 reaction generally by lowering the reaction energy barrier. Presence of a catalyst can cause problems because a catalyst can cause "pre-cure" of the resin, which

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as a too-rapid onset of the polymerization reaction characterized by excessive polyurea formation after impregnating the cellulosic material but before heat and pressure is deliberately applied for curing. Pre-cure can cause inconsistent product quality and/or general degradation of physical parameters such as 5 internal bond strength compared to composites made without a catalyst. Hence, use of a catalyst can make the overall process difficult to control. However, if pre-cure can be controlled or at least limited, composites having acceptable industrial properties can be produced according to the present invention.

If used, the catalyst can be selected from a variety of catalysts used 10 for isocyanate polymerizations. The amount of catalyst is preferably within the range of 0.1 to 0.5% w/w, relative to the mass of the resin. Possible catalysts include aliphatic tertiary amines such as 1,4-diazobicyclo-(2,2,2)-octane ("DABCO"), aliphatic metal complexes such as dibutyltin dilaurate or tin octoate, and acetyl acetones.

15 The liquid resin is applied to the cellulosic material in any manner whereby satisfactory impregnation of the cellulose fibers by the resin can be achieved. Typical loading levels are within the range of about 8 to about 20% resin relative to the mass of the cellulose, which yields composites exhibiting 20 excellent end-use properties at reasonable manufacturing costs. In the usual case where the cellulosic material is in sheet form, the resin can be applied on one or both sides of each sheet by spraying, dipping, rolling, or other suitable process known in the art.

The cellulosic material can be impregnated via either a batch or 25 continuous process, each employing different types of machinery. A continuous process is especially suitable when the cellulosic material is provided in the form of a continuous roll, such as with various papers and linerboard stock. For continuous impregnation, a two-roller applicator (size press) is an effective means for applying resin to the cellulosic material, wherein the cellulosic material is fed through a continuous bead or resin lying in the nip zone of two press rollers 30 which force the resin into the fiber matrix of the cellulosic material. Other effective means for applying the resin to the cellulosic material include a gravure

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roll-coater and a dip-bath containing the resin through which the cellulosic material is passed.

Using sheetlike or matlike cellulosics as examples, the resin can be applied to either the wire side or the felt side of the sheet, or to both sides. In 5 any event, it is important that the resin be applied in a manner that will ensure full and substantially uniform penetration of the resin throughout the "Z" or thickness dimension of the sheet.

Satisfactory resin-impregnation of kraft linerboard sheets results in a resin loading of about 10-20% w/w relative to the mass of the linerboard. In 10 fact, the resin loading of 58- and 69-lb linerboards is consistently about 15-16% when applied using a gravure roll-coater apparatus known in the art. Resin-loading values either greater or less than the 10-20% range may result when other types of cellulosic material are impregnated, depending on a number of factors including porosity, density, fiber geometry, thickness, rigidity, and 15 hyrophilicity of the cellulosic material, as well as the type of resin-impregnation machinery used. Gravure roll-coaters work well for linerboards and other paper-like cellulosic materials.

Once the cellulosic material has been impregnated with the polyisocyanate resin, the impregnated sheet is cured by simultaneous application 20 of heat and pressure for a time not exceeding about five minutes. The curing temperature can be within the range of about 105° to about 245°C; and the pressure within the range of about 130 to about 1200 psig. Shorter times are generally used with making thinner composites. The cited ranges of temperature and pressure are sufficient to effect polymerization of the polyisocyanate to form 25 polyurea and, at the same time, to effect possible covalent bonding of the polyisocyanate molecules to the cellulose molecules.

Since heat and pressure are required to initiate curing, impregnated cellulosic material can be stored for short periods of time, up to several days, before curing. Storage should be at about room temperature.

30 The polyurea-cellulose composite according to the present invention can be made having only one ply produced by curing only a single lamina of

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polysisocyanate-impregnated cellulosic material. The polyurea-cellulose composite can also be made having multiple plies, produced by curing a laminarily stacked arrangement of polysisocyanate-impregnated cellulosic material. Such multiple-ply composites generally are thicker and more rigid than single plies. Due to their thickness, multiple-ply composites usually must be cured at higher pressures within the stated range than single-ply composites, where the higher pressure ensures good interply contact and adhesion during curing.

Curing can be performed as either a continuous or as a batch process. Platen presses known in the art are generally used for batch-cured flat sheet-like composites. A possible disadvantage with using such presses is the requirement for extreme flatness and parallel orientation of the caul plates. Misoriented or non-flat plates can result in composites having non-uniform properties. Nevertheless, caul-plate presses are often used to make sheet products measuring 4x8 or 4x4 feet. Continuous presses, on the other hand, are generally able to produce the same degree of curing using lower curing pressures than caul-plate presses. Also continuous presses allow long sheets of product to be made having substantially uniform properties.

Polyisocyanate-impregnated cellulosic material according to the present invention can also be applied to a rigid substrate. Both single and multiple plies can be applied to at least one surface of the substrate. The curing step comprises heating and pressuring both the substrate and polysisocyanate-impregnated cellulosic together so as to effect bonding of the impregnated cellulosic to the substrate. Preferably, the rigid substrate is a cellulosic material such as wood, wood veneer, reconstituted wood product, wood-containing composite, or the like. When cured, the resulting polyurea-cellulose composite provides a durable "skin" bonded to the substrate.

The following Examples are provided to illustrate the invention in accordance with the principles of this invention but are not to be construed as limiting the invention in any way.

30

Example 1

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In this Example, the effect on viscosity of adding particular amounts of propylene carbonate to PMDI was investigated. Propylene carbonate was added to PMDI at a concentration of 1%, 5%, 10% and 15% w/w relative to the PMDI. The control was neat (undiluted) PMDI. After adding the polypropylene 5 carbonate, the viscosity of each resin mixture was determined at 22.5°C. Figure 1 is a histogram of the results, showing that, for example, the viscosity of a PMDI resin containing 15% propylene carbonate was less than half that of neat PMDI or of a resin containing only 1% propylene carbonate.

10 Example 2

In this Example, a qualitative investigation was made of the degree of penetration into kraft linerboards of either neat or diluted PMDI resin. Single kraft linerboard sheets having 58-lb basis weight and about 5-7% moisture content were impregnated with PMDI, either in neat form or diluted with 5, 10 15 or 15% w/w propylene carbonate. The PMDI resin was applied to the linerboard using a two-roll applicator (size press). The linerboard was fed through the bead and between the rollers such that the resin was applied simultaneously to both surfaces (wire and felt sides) of the linerboard. The amount of resin impregnated into the linerboard was governed in part by the rotational velocity of the rollers 20 and the pressure (clearance) between the rollers.

The resin-impregnated sheets were cured by oven heating at 177°C for 3-4 hours without pressurization. After cooling, the sheets of polyurea-cellulose composite were cross-sectioned and the sections examined under the light microscope.

25 Figure 2A shows a cross-sectional view depicting the "Z" or thickness dimension of a single-ply composite sheet made using neat PMDI. The core (or center) portion of the linerboard has a lower amount of polyurea than the outer portions near the surfaces. This result indicates that, as neat PMDI is applied to the surfaces of the linerboard, penetration of the PMDI to the 30 linerboard core is limited, due in part to the relatively high viscosity of neat

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PMDI. As a result, most of the PMDI remains near the surfaces of the linerboard.

Figure 2B shows a sheet of polyurea-cellulose composite made using PMDI diluted with 5% propylene carbonate. The resin has penetrated more 5 deeply through the Z dimension of the linerboard. As a result, the core portion of the linerboard has a greater amount of polyurea than the core portion of the linerboard of Figure 2A. However, Figure 2B shows that a greater amount of polyurea is still present in the outer portions of the linerboard than in the core.

In Figures 2C and 2D, showing single-ply polyurea-cellulose 10 composite sheets made using PMDI diluted with 10% and 15% propylene carbonate, respectively, an apparently uniform distribution of polyurea is present throughout the Z dimension of the linerboard.

Therefore, the results shown in Figures 2A-2D indicate that, in order to ensure a substantially uniform distribution of polyurea throughout the 15 Z dimension of linerboards, PMDI should be diluted with at least 10% w/w propylene carbonate or similar solvent. Uniform impregnation of other types of cellulosic material may require more or less solvent in the resin.

Example 3

20 In this Example, the distribution of PMDI resin through the Z dimension of kraft linerboard was quantitatively investigated. PMDI was applied to kraft linerboard sheets (58-lb basis weight; 5-7% w/w residual moisture content) using one of two methods. In the first method, PMDI was applied by dipping single sheets of the linerboard in a solution of 13% w/w PMDI in acetone 25 until the linerboards were saturated (12-14% w/w resin loading). The saturated sheets were then hung vertically for a sufficient time to allow the solvent to evaporate. In the second method, neat PMDI was applied to either the wire side, the felt side, or both sides of single plies of kraft linerboards. The neat resin was applied using a two-roller coater where the linerboard was passed through a bead 30 of the liquid resin situated on either one or both sides of the linerboard as it is passed between the rollers. In one instance, all the resin was applied to the wire

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side of the linerboard; in another instance, all the resin was applied to the felt side; in yet another instance, the resin was simultaneously applied to both sides of the linerboard. Resin-impregnated sheets were cured by oven heating at 177°C for 3-4 hours without application of external pressure.

5 After curing, two-thirds of the thickness of each sheet were carefully ground away, leaving only a one-third thickness section representing the wire side, the felt side, or the center (core) of the polyurea-cellulose composite sheet. Since cured PMDI is a polyurea which includes nitrogen atoms integrated into the polymer matrix, each ground section was analyzed for nitrogen content using
10 the Kjeldahl method, the results of which yielded a useful quantitative measure of the relative amount of polyurea therein and, therefore, the degree of penetration of the resin into the linerboard.

Briefly, to perform the Kjeldahl procedure, portions of each section
15 were cut to pieces weighing about 2 grams each and carefully weighed to \pm 0.1 g. Each piece was transferred to a 500 mL Kjeldahl flask. Additional flasks were prepared for reference samples and controls. To each flask were added 15.0 g K₂SO₄ and about 5 boiling chips, then 30 mL of a digest mixture (6.00 g SeO₂ in 24 mL ammonia-free water, plus 1800 mL of concentrated H₂SO₄). Each flask was mounted on a cool Kjeldahl digestion apparatus. The heating controls on
20 the apparatus were turned on low and digestion allowed to proceed until the contents of the flask became fully liquid. Temperature was then increased to boiling which was allowed to continue until the solution became clear, then continued for an additional 20 minutes. After allowing the flask to cool, 50 mL ammonia-free water was slowly added while swirling the flask, using the water to wash down debris on the inside walls of the flask and dissolving any salt sediment.
25 The liquid was transferred to a 250 mL volumetric flask, which was filled to volume with cool liquid from three additional rinsings of the Kjeldahl flask using ammonia-free water. A 5.00 mL aliquot of the liquid in the volumetric flask was added to a 100 mL mixing cylinder. The aliquot was diluted to about 90 mL with
30 ammonia-free distilled water, then 3 mL of 20% NaOH was added and the resulting solution brought to volume by adding additional water. The contents

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of the cylinder were transferred to a 150 mL beaker containing a stirring bar. With stirring, ammonia concentration was determined using an ammonia electrode at steady state both before and after adding 10 mL of 20.0 mg/L $\text{NH}_4\text{-N}$ standard solution.

5 Figure 3 shows that 13% w/w of PMDI in acetone results in a desired substantially uniform distribution of the resin throughout the wire side, the felt side, and the core of the linerboard when the resin is applied simultaneously to both sides of the linerboard. Application of neat PMDI simultaneously to both sides of the linerboard resulted in substantially less
10 polyurea in the core and relatively more polyurea in the felt and wire sides of the linerboard. Application of neat PMDI to only the felt side resulted in a very low relative amount of polyurea on the wire side; likewise, application of neat PMDI to only the wire side; likewise, application of neat PMDI to only the wire side resulted in a very low relative amount of polyurea on the felt side. It is possible
15 that other types of coaters would produce somewhat different results.

Example 4

In this Example, the internal bond strengths of 3-ply polyurea-cellulose composite sheets made using either 58-pound or 69-pound kraft linerboards were evaluated. Each linerboard was impregnated with a loading level of about 16% w/w PMDI resin in either neat form or diluted with 2, 10 or 20% w/w propylene carbonate in the presence or absence of a catalyst. When present, the catalyst was diazobicyclooctane (DABCO), prepared as a 0.05% solution in acetone, with which solution the linerboards were first impregnated, then dried, then subsequently impregnated with the PMDI resin. After impregnation, three linerboards were plied and cured by heating to 204°C and pressurizing momentarily at 400 psi, opening momentarily to atmospheric pressure, then pressurizing at 800 psig for 40 seconds at the same temperature. If no catalyst was used, the linerboards were impregnated with the PMDI resin, then cured.

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18 Eighteen samples of 3-ply polyurea-cellulose composite sheets were prepared for testing purposes from each combination of linerboard basis weight percent of propylene carbonate, and presence or absence of a catalyst. Testing was performed according to ASTM test specification number D1037-89, 5 paragraphs 28.1-33. Each sample was cut to a square shape having 2 inch sides. Each square surface was cemented to an identically-sized surface of a steel block using cyanoacrylate or epoxy cement. After the cement cured, each block was grasped in an opposing coaxial jaw of an Instron device adjusted to apply a force tending to pull the blocks away from each other. The force at which each sample 10 pulled apart was recorded.

20 Test results are shown in Figures 4A and 4B, where the data points represent sample means ($n = 18$) and the brackets represent \pm one standard deviation from the corresponding mean. Figure 4A, internal bond values for the combination of uncatalyzed resin and 58-lb linerboard increased with increasing 15 content of propylene carbonate, from about 530 psi with neat PMDI to about 1150 psi with 20% propylene carbonate. With catalyzed resin, addition of propylene carbonate yielded an increase in internal bond strength, but the magnitude of the increase over neat PMDI was not as pronounced as with no catalyst. Nevertheless, the magnitude of the increase in internal bond strength 20 with 2% to 20% propylene carbonate was about the same for both catalyzed and uncatalyzed resin.

25 Figure 4B shows internal bond data for polymer cellulose made using 69-lb basis weight linerboard and uncatalyzed resin. Again, addition of propylene carbonate to the PMDI resin yielded a general increase in internal bond strength, where the strength obtained using 20% propylene carbonate was about double the strength obtained using neat PMDI.

Example 5

30 In this Example, evaluations were made of the tensile strengths of various polyurea-cellulose composite sheets made using either neat PMDI or PMDI diluted with up to 20% w/w propylene carbonate, either with or without

- 20 -

a catalyst (DABCO). Three-ply composite sheets were made using either 58-lb or 69-lb basis weight kraft linerboards. Eighteen samples were prepared for each combination of basis weight, percent dilution, and presence or absence of catalyst, essentially as described in Example 4. After curing, the samples were each cut 5 to the "dogbone" shape appropriate for tensile testing. Tensile testing was performed in the "machine direction" (MD) using an Instron device according to ASTM test specification number D638-89.

As used herein, the "machine direction" or "MD" refers to the net orientation of cellulose fibers in a sheet of cellulosic material such as paper. For 10 example, when paper is made using conventional roller machinery, the cellulose fibers tend to become longitudinally oriented in a direction substantially parallel to the direction of movement of the paper through the roller apparatus. The finished paper tends to show less resistance against a tensile force applied perpendicularly to the machine direction (i.e., in the "cross direction" or "CD") 15 compared to tearing forces applied in the machine direction.

Test data are plotted in Figures 5A and 5B, pertaining to 58-lb linerboard, and in Figures 5C and 5D, pertaining to 69-lb linerboard. Data points represent sample means ($n = 18$) and brackets represent \pm one standard deviation from the corresponding mean.

20 In Figure 5A, dilution of catalyzed PMDI with up to 20% propylene carbonate caused an almost negligible decrease in tensile strength of the composite, as measured in the machine direction. Uncatalyzed PMDI generally yielded composite sheets having higher tensile strength values than sheets made with catalyzed PMDI. Nevertheless, the tensile strength of sheets made using 25 PMDI with 20% propylene carbonate is within 5% of the tensile strength of sheets made using neat PMDI.

Figure 5B shows data pertaining to the percent elongation experienced by the samples of Figure 5A during tensile testing between a no-load condition and just before undergoing tensile fracture. Such data is useful as an 30 indication of product brittleness. Almost all samples, whether catalyzed or not, experienced a percent elongation between about 2.2 and 2.4% before breaking.

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Figure 5C shows data similar to the uncatalyzed data shown in Figure 5A but obtained using composite sheets made with 69-lb basis weight linerboards. As can be seen, dilution of uncatalyzed PMDI with 20% w/w propylene carbonate yielded an increase in tensile strength over neat PMDI.

5 Figure 5D shows data similar to the uncatalyzed data shown in Figure 5B but obtained using composite sheets made with 69-lb basis weight linerboards. Dilution of uncatalyzed PMDI seemed to result in no apparent change in percent elongation of the composite sheets during tensile testing.

10 Example 6

In this Example, an evaluation was made of the effect on modulus of rupture and modulus of elasticity of polyurea-cellulose composite made using either neat PMDI or PMDI diluted with up to 20% w/w propylene carbonate, either with or without a catalyst (DABCO). The samples were prepared as 15 described above in Example 5.

Modulus of rupture tests were performed according to ASTM test specification number D790-86 ("flexural strength"). Modulus of elasticity tests were performed according to the same test specification.

20 Test data pertaining to modulus of rupture area shown in Figures 6A and 6B; test date pertaining to modulus of elasticity are shown in Figures 6C and 6D. Data points represent sample means ($n = 18$) and brackets represent \pm one standard deviation from the corresponding mean.

25 In Figure 6A, showing data obtained from polyurea-cellulose composite sheets made using 58-lb basis weight linerboards, increasing dilution of uncatalyzed PMDI resin with up to 20% w/w propylene carbonate resulted in an increase in the modulus of rupture, from about 19000 psi from composite made using neat PMDI to greater than 21000 psi from composite made using PMDI containing 20% w/w propylene carbonate. Similar dilution of catalyzed PMDI, in contrast, yielded a corresponding decrease in modulus of rupture. The 30 general increase in modulus of rupture upon diluting uncatalyzed PMDI is also evident in Figure 6B, showing data obtained with composite made using 69-lb

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basis weight linerboards. Comparison of the uncatalyzed data of Figures 6A and 6B indicates that the modulus of rupture is dictated by the characteristics of the PMDI resin and not by the basis weight of the linerboard.

The data pertaining to modulus of elasticity shown in Figures 6C and 6D show trends similar to those of Figures 6A and 6B. Up to a 20% w/w dilution of uncatalyzed PMDI resin with propylene carbonate, compared with neat uncatalyzed PMDI, resulted in an increase in the modulus of elasticity. Dilution of catalyzed PMDI, in contrast, resulted in a corresponding decrease in the modulus of elasticity. Again, these parameters seemed to depend more on the characteristic of the PMDI resin (diluted versus undiluted; catalyzed versus uncatalyzed) rather than the basis weight of the linerboard.

Example 7

In this Example, several types of catalysts were evaluated, including 15 a tertiary amine (DABCO, Aldrich Chemical Co.) and dibutyltin dilaurate (Air Products 5-12), when used with PMDI. Both are frequently used in the art when making polyurethane. With respect to the dibutyltin dilaurate, an impregnating resin was prepared by mixing together propylene carbonate (Texaco; 10% w/w based on mass of PMDI), dibutyltin dilaurate (0.05% w/w based on mass of 20 PMDI), and PMDI (Dow Chemical PAPI 2027). Unbleached linerboards having 58-lb basis weight were impregnated with this resin using a roller applicator. Resin loading was 14% w/w relative to the mass of the linerboard.

Three-ply composite panels were made during 3-ply stacks of impregnated linerboards at 204°C and the following pressurization sequence:

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	close to 400 psig	12 sec
	hold at 400 psig	2 sec
	open to atmospheric	8 sec
	close to 800 psig	10 sec
5	hold at 800 psig	30 sec
	open to atmospheric	6 sec

When the first open to atmosphere was maintained for only 6 seconds, a number of panels acquired "blows" (bubbling), rendering them untestable.

10 With respect to the DABCO, a first set of composite panels was produced by the following procedure: 1 gram DABCO was dissolved in 20 g propylene carbonate, to which was added PMDI to 200 grams. A white precipitate formed. After stirring of the resin, unbleached 58-lb linerboard was impregnated with the resin. Three-ply composite panels were made using the 15 same procedure as described above for the dibutyltin dilaurate-containing resin. The panels lacked adequate interply bonding and were untestable, apparently because pre-cure occurred. When the curing temperature was lowered to 149°C with the pressurizing profile left unchanged, interply adhesion improved, yielding a second set of panels that were testable.

20 A third set of panels was produced by first impregnating 58-lb unbleached linerboards with a 0.5% w/w solution of DABCO in acetone, then allowing to dry overnight. The DABCO-containing linerboards were then impregnated with a resin comprising PMDI and 10% w/w propylene carbonate using a roller applicator. Resin loading was 26% w/w relative to the mass of the 25 dry DABCO-impregnated linerboard.

Three-ply composite panels were made by curing 3-ply stacks of impregnated linerboards at 204°C and a pressurization sequence similar to that for the dibutyltin-dilaurate-catalyzed boards except that the hold at 800 psig was increased to 40 seconds. The resulting panels were well-bonded.

30 When the above panels were tested, the following results were obtained:

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TABLE I

Set	Catalyst	Tensile Strength	Flexure	Flex Modulus	Internal Bond
5	1	dibutyltin	22685 psig	-	241 psig
	2	DABCO	17523 psig	-	63 psig
	3	DABCO	17112 psig	1.5x10 ⁸	373 psig

10 In Table I, the presence of a catalyst in the resins of Sets 1 and 2 appeared to detrimentally influence the mechanical properties of the composite panels. This was evidenced by the "blows" in Set 1 panels produced with a 6-second first open to atmospheric pressure, and by the lack of interply adhesion in Set 2 panels unless the cure temperature was reduced from 204°C to 149°C.

15 This implies that varying degrees of pre-cure occurred, yielding reduced strength. Even the internal bond strength of Set 1 panels is low compared to what would be expected for a resin containing propylene carbonate. The internal bond strength of Set 3 is improved over Sets 1 and 2 and may reflect the fact that the catalyst was preapplied to the sheet before application of the PMDI resin,

20 thereby minimizing the time that PMDI and the catalyst were together before curing. Set 3 also exhibited twice the resin loading level (relative to Set 2) which should result in improved physical properties, even though the tensile strength is lower than expected.

Having illustrated and described the principles of my invention in several preferred embodiments and multiple examples, it should be apparent to those skilled in the art that the invention can be modified in arrangement and detail without departing from such principles. I claim all modifications coming within the spirit and scope of the following claims.

I CLAIM:

1. A method for making a polyurea-cellulose composite which comprises:

5 impregnating a substantially delignified cellulosic material with an isocyanate resin comprising at least one polyisocyanate compound and a miscible organic solvent therefor, where the solvent comprises up to about 20% w/w of the polyisocyanate and the isocyanate resin constitutes about 8% to about 20% w/w of the cellulosic material so as to form a polyisocyanate-impregnated cellulosic material; and

10 curing the polyisocyanate-impregnated cellulosic material at a temperature within a range of about 105° to about 245°C for a time not exceeding about 5 minutes and at a pressure within a range of about 130 to about 1200 psig.

15 2. The method of claim 1 in which the cellulosic material is in a sheet form having first and second sheet surfaces substantially parallel to each other and a Z or thickness dimension extending in a direction between the first and second sheet surfaces, and wherein the isocyanate resin is substantially uniformly distributed throughout the Z or thickness dimension of the sheet after 20 impregnating the sheet with the isocyanate resin.

3. The method of claim 1 in which the polyisocyanate is selected from the group consisting of lower aliphatic, alicyclic, and aromatic polyisocyanates, and mixtures thereof.

25 4. The method of claim 3 in which the polyisocyanate is poly(diphenylmethane diisocyanate).

5. The method of claim 1 in which the solvent is selected from the group consisting of the alkylene carbonates, aromatics, halogenated aromatics, nitroaromatics, alkylated aromatics, ethers, ketones, and alkyl acetates.

30 6. The method of claim 5 wherein the solvent is propylene carbonate.

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7. The method of claim 1 in which the cellulosic material has a moisture content not exceeding about 10% w/w relative to the mass of the cellulosic material.

8. The method of claim 1 in which the isocyanate resin includes
5 a catalyst.

9. The method of claim 8 in which the catalyst is present in the isocyanate resin in a concentration within a range of about 0.1 to about 0.5% w/w relative to the isocyanate resin.

10. The method of claim 8 in which the catalyst is selected from the group consisting of aliphatic tertiary amines, aliphatic metal complexes, and acetyl-acetonates.

11. The method of claim 10 in which the catalyst is selected from the group consisting of diazobicyclooctane, tin octoate, and dibutyltin dilaurate.

12. The method of claim 1 in which the cellulosic material is
15 selected from the group consisting of pulped cellulose fibers; chemical pulps; thermomechanical pulps; bleached and unbleached paper and paper-like materials, non-woven mats, sheets and felts.

13. The method of claim 1 in which the solvent comprises from about 5% w/w to about 20% w/w relative to the polyisocyanate.

20 14. The method of claim 13 in which the isocyanate resin includes a catalyst in a concentration within a range of about 0.1% to about 0.5% w/w relative to the isocyanate resin.

15. A method for making a laminated polyurea-cellulose composite material comprising the steps:

25 individually impregnating each of plural sheets of substantially delignified cellulosic material with an isocyanate resin comprising at least one polyisocyanate compound and a miscible organic solvent therefor, where the solvent comprises up to about 20% w/w of the polyisocyanate and the resin constitutes about 8 to about 20% w/w of the cellulosic material so as to form
30 plural polyisocyanate-impregnated cellulosic lamina;

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plying at least two of the polyisocyanate-impregnated cellulosic lamina together so as to form a laminar stack of said polyisocyanate-impregnated cellulose lamina; and

5 curing the stack of plied lamina at a temperature in a range of about 105°C to about 245°C for a time not exceeding about 5 minutes and at a pressure within a range of about 130 to about 1200 psig.

16. The method of claim 15 in which the polyisocyanate-impregnated cellulosic material is plied on at least one face of a rigid substrate.

17. The method of claim 16 in which the substrate is selected 10 from the group consisting of wood, wood veneer, reconstituted wood products, and wood-containing composites.

18. The method of claim 15 in which the cellulosic material is selected from the group consisting of pulped cellulose fibers; chemical pulps; thermomechanical pulps; recycled pulp fiber; bleached and unbleached paper and 15 paper-like materials, non-woven mats, sheets, and felts.

19. The method of claim 15 in which the polyisocyanate is selected from the group consisting of lower aliphatic, alicyclic, and aromatic polyisocyanates, and mixtures thereof.

20. The method of claim 19 in which the polyisocyanate is poly(diphenylmethane diisocyanate).

21. The method of claim 15 in which the solvent is selected from the group consisting of alkylene carbonates, aromatics, halogenated aromatics, nitroaromatics, alkylated aromatics, ethers, ketones, and alkyl acetates.

22. The method of claims 21 in which the solvent is propylene 25 carbonate.

23. The method of claim 15 in which the isocyanate resin includes a catalyst.

24. The method of claim 23 in which the catalyst is present in the isocyanate resin at a concentration of about 0.1 to about 0.5% w/w relative to the 30 isocyanate resin.

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25. The method of claim 24 in which the catalyst is selected from the group consisting of aliphatic tertiary amines, aliphatic metal complexes, and acetyl acetonates.

5 26. The method of claim 25 in which the catalyst is selected from the group consisting of diazobicyclooctane, tin octoate, and dibutyltin dilaurate.

27. The method of claim 15 in which the cellulosic material has a moisture content not exceeding about 7 percent w/w relative to the mass of the cellulosic material.

10 28. A polyurea-cellulose composite made by the method of claim 1.

29. A laminated poly-urea composite made by the method of claim 15.

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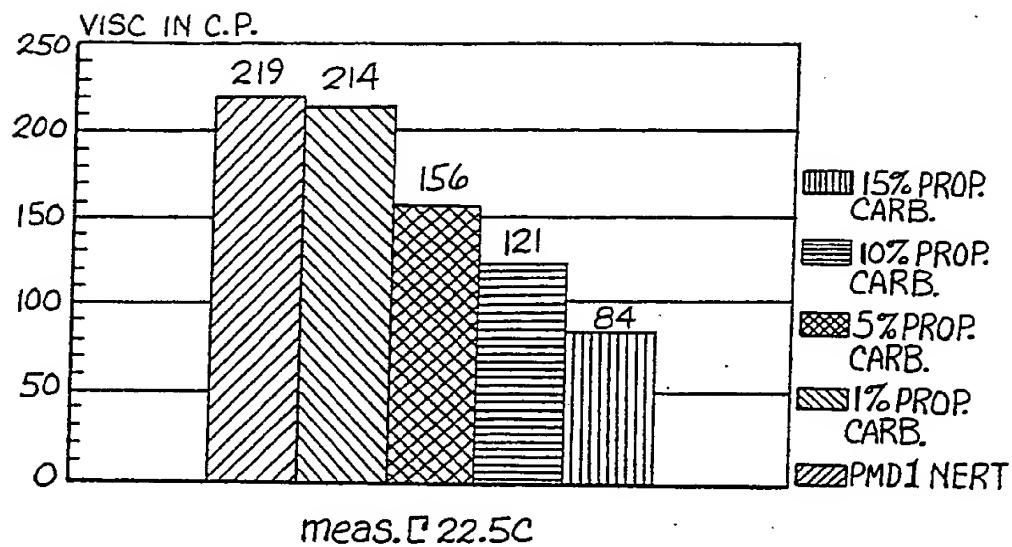
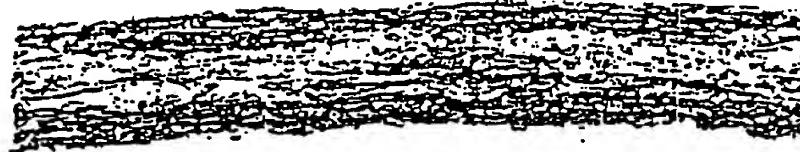
*Fig. 1**Fig. 2A**Fig. 2B*

Fig. 2C

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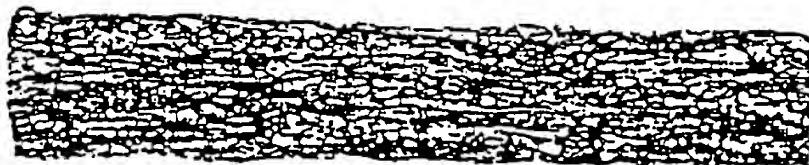
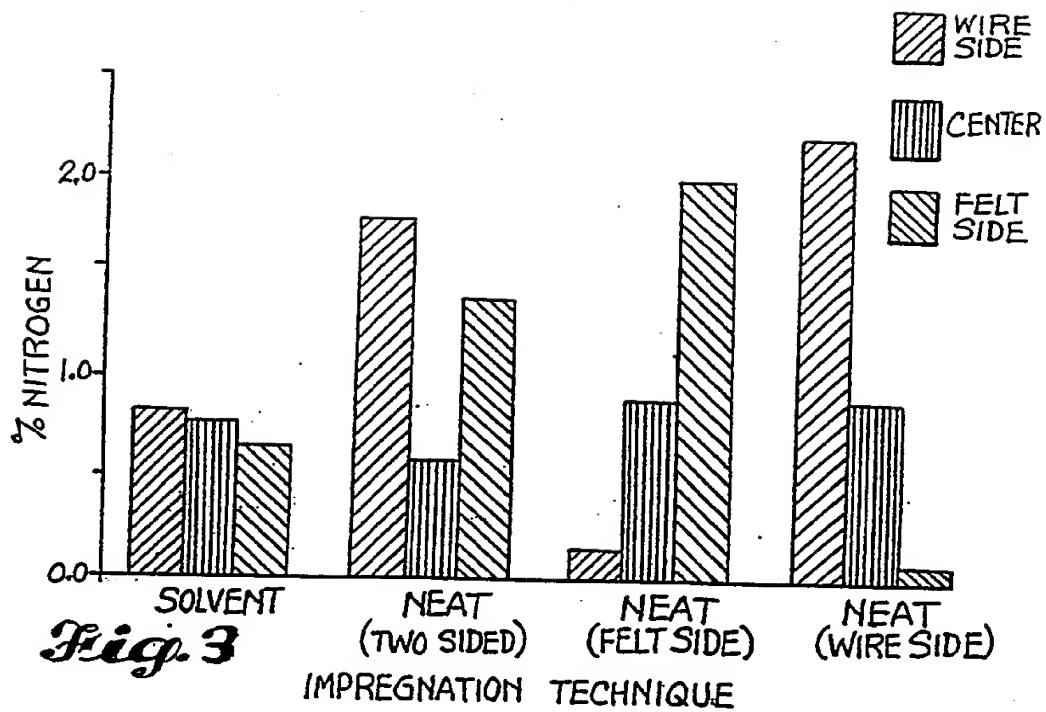


Fig. 2D



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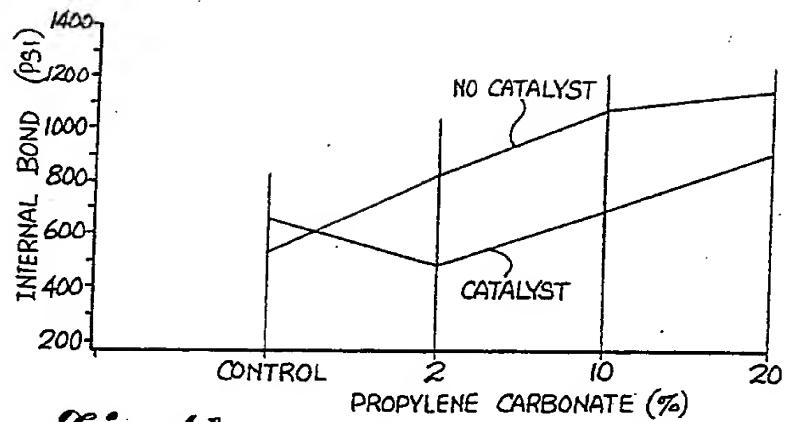


Fig. 4A

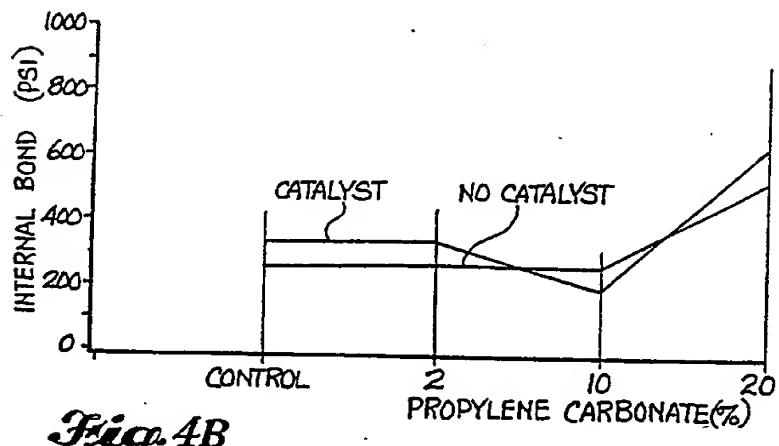


Fig. 4B

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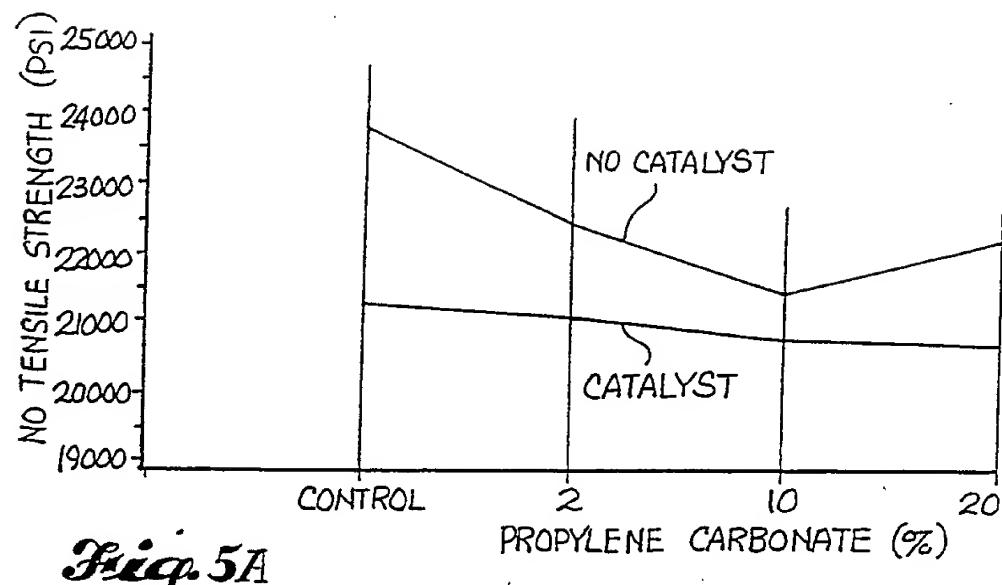


Fig. 5A

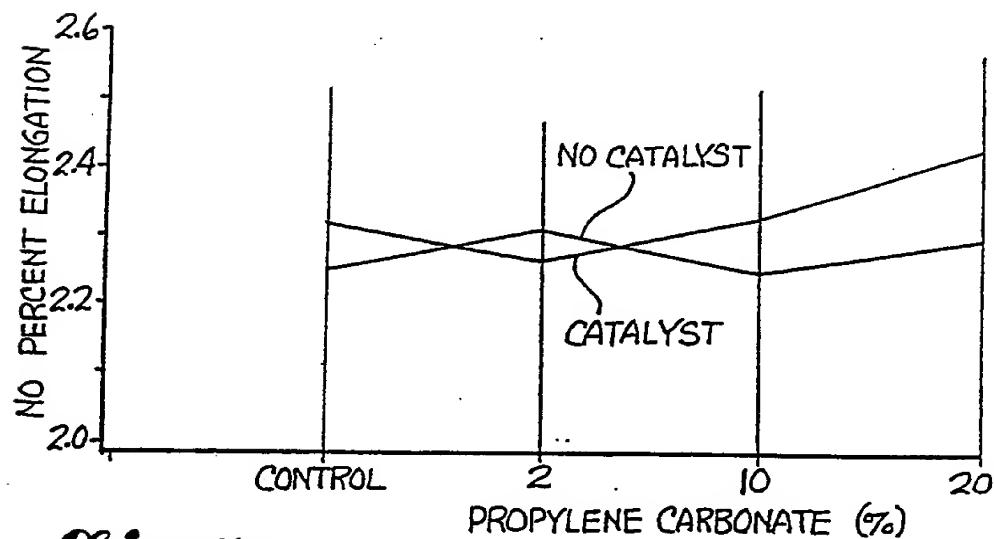


Fig. 5B

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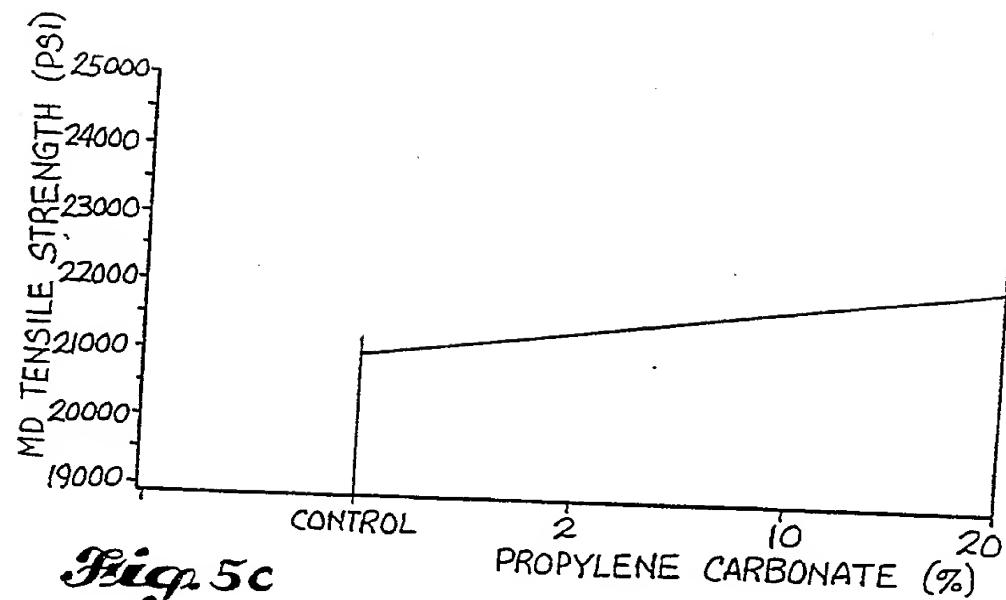


Fig. 5c

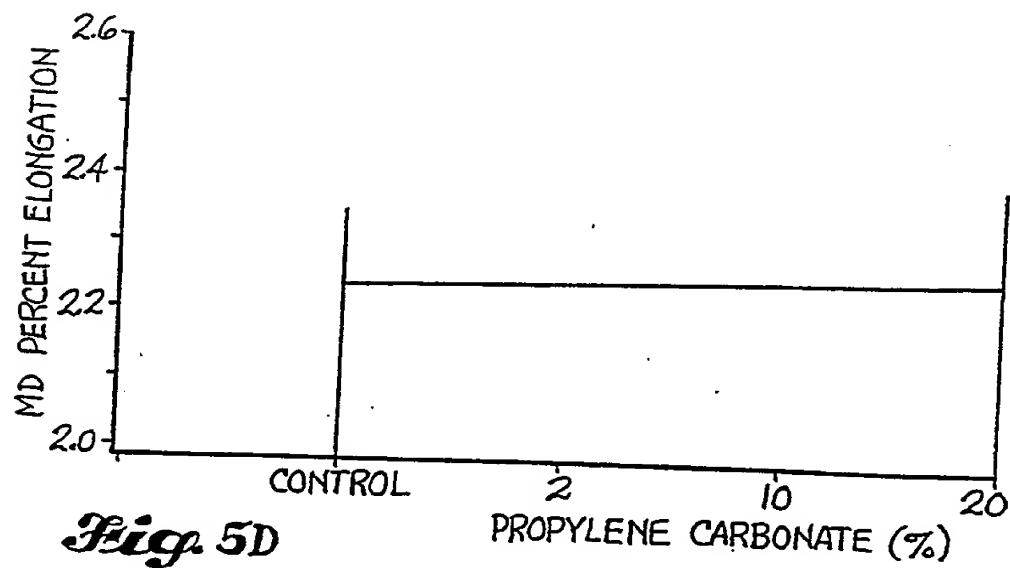
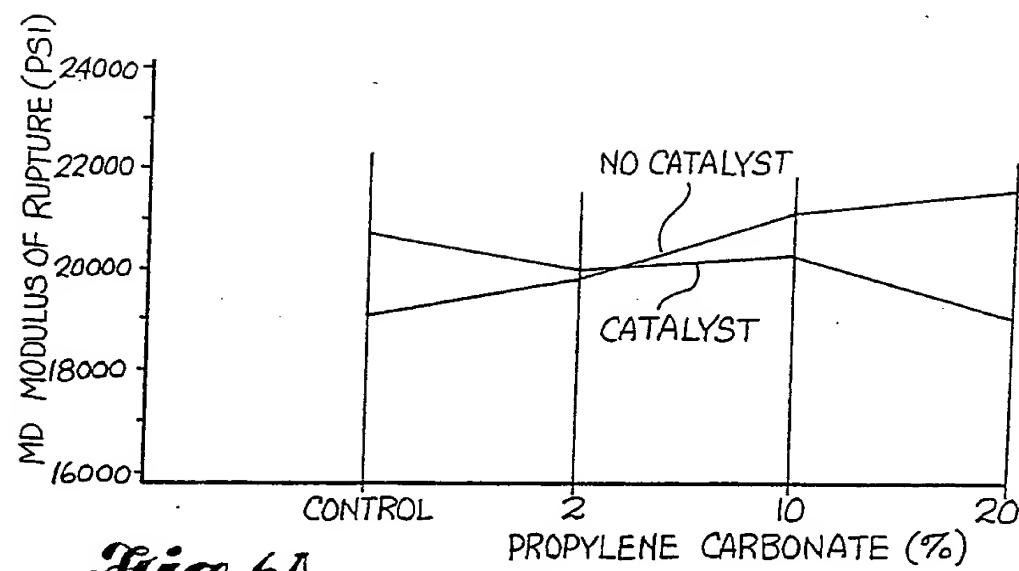
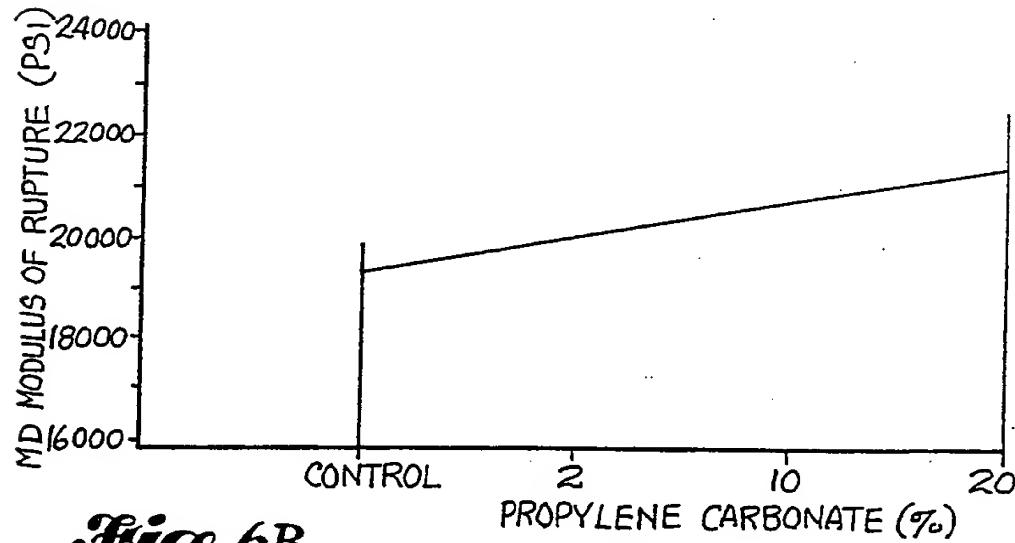


Fig. 5d

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*Fig. 6A**Fig. 6B*

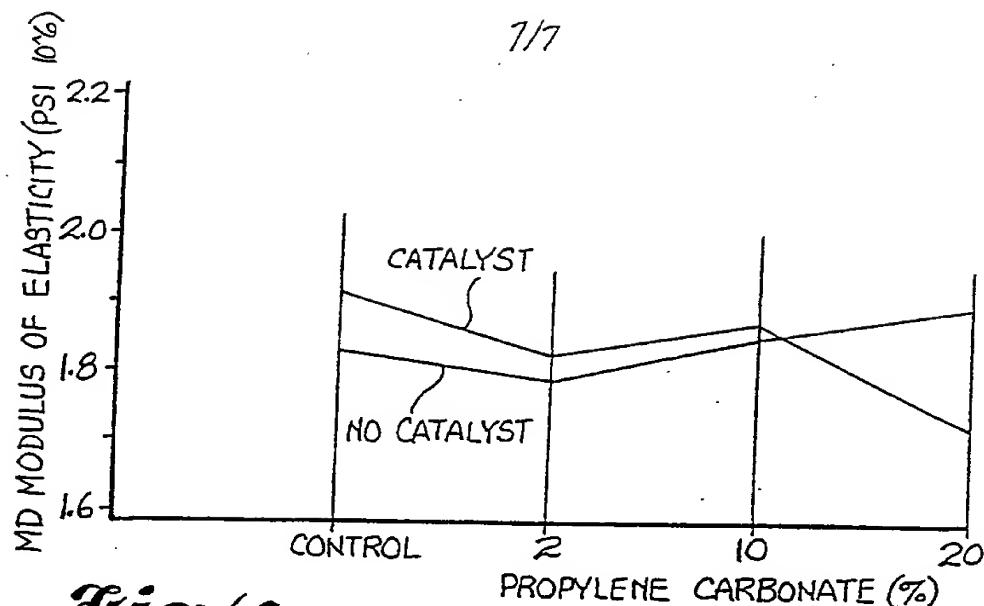


Fig 6C

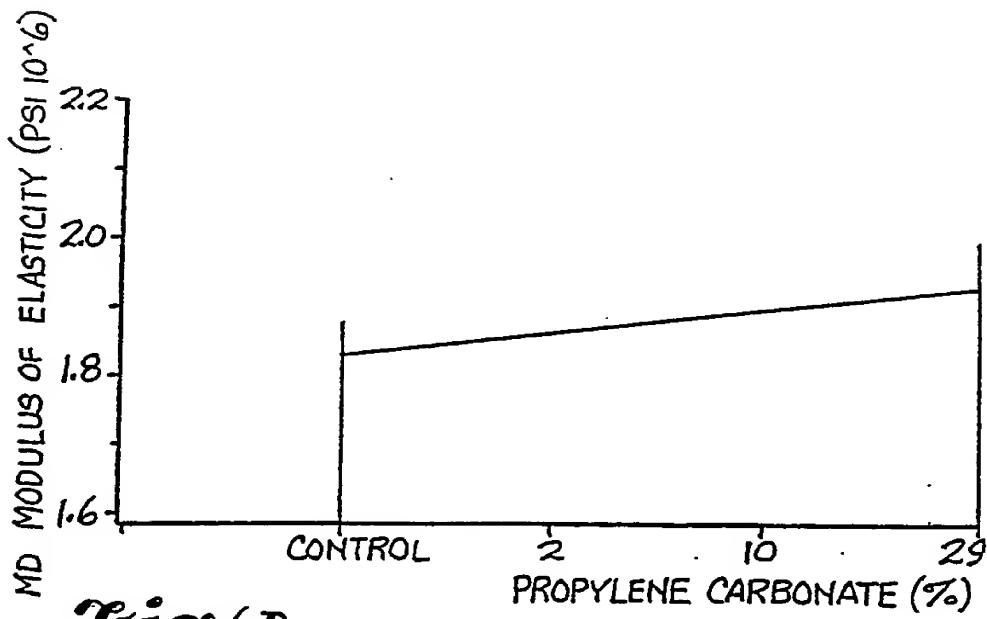


Fig 6D

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 91/07812

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶According to International Patent Classification (IPC) or to both National Classification and IPC
IPC5: C 08 G 18/08, 18/64, C 08 L 97/02, B 32 B 21/04

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
IPC5	C 08 G; C 08 L

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP, A1, 0304273 (ARCO CHEMICAL COMPANY) 22 February 1989, see the whole document	1-29
A	US, A, 3666593 (U.S. PLYWOOD-CHAMPION PAPERS INC.) 30 May 1972, see the whole document	1-29
P,X	US, A, 5008359 (FRANK R. HUNTER) 16 April 1991, see the whole document	1-29

* Special categories of cited documents:¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

23rd March 1992

Date of Mailing of this International Search Report

- 3. 04. 92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

Maria Peis

Maria Peis

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/US 91/07812

SA 54875

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 28/02/92.
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0304273	22/02/89	JP-A- US-A-	1082930 4879164
US-A- 3666593	30/05/72	NONE	
US-A- 5008359	16/04/91	NONE	

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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